WGC Technical Database – an immediate success!

The WGC Technical Database (see *Gold Bulletin*, vol 35 (**3**) 2002, page 100) went live on the WGC web site in August. It has proved an immediate hit with scientists and industrialists wanting to keep up-to-date with the latest science and technology of gold. Statistics show about 35,000 visits were made in September and this grew to almost 50,000 visits in October, a month-on-month increase of 14%. Updated quarterly, this searchable Database will next be updated at the end of this year.

Gold Bulletin is also available on the WGC website and is receiving around 9,000 visits per month. The Technical Database will be found at www.gold.org/value/sci_indu/techdatabase

Highlights from Recent Literature

Note:
A more comprehensive list of literature and patents, updated quarterly, will be found in the searchable **Technical Database** on the World Gold Council website, **www.gold.org** under the Science and Industry domain.

1 Analytical

1.1 A Photoelectron Spectroscopy study of Ethylenedioxythiophene Adsorption on Polycrystalline Gold Surfaces

The interaction between thin films of ethylenedioxythiophene (EDOT) and polycrystalline copper and gold surfaces was studied by J. Birgerson, M. Keil, A.W.D. Van der Gon, X. Crispin, M. Logdlund and W.R. Salaneck from the Department of Physics, Linkoping University, Linkoping, Sweden, *Materials Research Society Symposium Proceedings* 2001, **660** (Organic Electronic and Photonic Materials and Devices), JJ5.29/1-JJ5.29/6 using photoelectron spectroscopy.

Vapour deposition was used to prepare thick films of EDOT (approximately.100 .ANG.) onto clean gold surfaces. These were cooled down to a temp. of 170 K during the deposition process. Monolayers were prepared by slowly heating the thick films up to 300 K. At 300 K most of the material has evaporated from the surface and about one monolayer remains chemisorbed on the gold surface. This shows that there is an interaction between EDOT and gold.

This chemisorption causes a shift of approximately -0.5 eV of the binding energies for the core level electrons, presumably because of screening of the core-hole by the metal. An experimental and theoretical analysis of the valence level electrons suggests that two MOs, localised at the thiophene part of the molecule, are involved in the interaction with the metal atoms of the surface. The most likely orientation of the EDOT molecules is parallel to the gold surface. Upon adsorption the work function is changed from 5.2 eV for the clean gold surface to 4.0 eV for the EDOT monolayer. In the case of EDOT adsorbed on clean copper surfaces, no interaction was observed.

1.2 Application in Modern Instrumental Analysis Method of Nickel Sulphide Fire Assay Pre-concentration of Platinum Group Elements and Gold

This article by X. Liu and S. Dong, from the Kunming Institute of Precious Metals, Peoples Republic of China, *Guijinshu* 2002, **23**(1), 45-52, reviews the current analytical detection methods for trace and ultra trace precious metals. Precious metals are initially collected by nickel sulphide fire assay, then detected by neutron activation analysis, inductively coupled plasma-mass spectrometry, atomic absorption spectrometry and atomic emission spectrometry methods. The mechanisms for nickel sulphide fire assay collecting precious metals were discussed. According to crystal structure and thermodynamic data of precious metals sulphide and compounds in silicate phase, precious metals tend to be in nickel sulphide phase when nickel sulphide phase is separated from the silicate phase.

1.3 Characterisation of the [Ru(Cn)5(pyS)]4- Ion Complex Adsorbed on Gold, Silver and Copper Substrates by Surface-Enhanced Raman Spectroscopy

The adsorption of the [Ru(CN)5(pyS)]4- (pyS=4-mercaptopyridine) ion complex on gold, silver and copper surfaces has been studied by surface-enhanced Raman spectroscopy (SERS). P. Corio, G.F.S. Andrade, I.C.N. Diogenes, I.S. Moreira, F.C. Nart and M.L. A. Temperini from Instituto de Quimica, Universidade de Sao Paulo, Brazil, *Journal of Electroanalytical Chemistry* 2002, **520**(1-2), 40-46. The influence of the nature of the metallic substrates in the adsorption geometry of the complex is reflected in a strong variation of the SERS spectra. In particularly, the relative intensities of characteristic vibrational modes of pyS and CN ligands, which is likely to result from changes in specific chemical interactions involving both ligands and the surface. The effect of the surface modification procedure on the properties of the

adsorbed monolayers has also been investigated for the gold surface. Surface modification has been performed by self-assembly or under an electrochemical potential. The spectroscopic results have shown that, according to the modification procedure, the modifier can be bound to the surface via sulphur atom or via CN nitrogen atoms. The ability to control the orientation of the adsorbed monolayer permits control over the properties of the interface, as demonstrated by the study of the electrochemistry of cytochrome-c (cyt-c) on the differently prepared surfaces. A reversible electrochemical response of the metalloprotein is only observed on the self-assembly prepared surface, where CN moieties of the surface modifier are available to interact with the protein molecule.

2 Catalysis

2.1 Simultaneous Presence of Cationic and Reduced Gold in Functioning MgO-Supported CO Oxidation Catalysts: Evidence from X-Ray Absorption Spectroscopy

Gold clusters on the surface of MgO powder (calcined at 673 K) were prepared from adsorbed [$Au(CH_3)_2$(acac), where acac is $C_5H_7O_2$] and characterised by extended X-ray absorption fine structure (EXAFS) spectroscopy and X-ray absorption near edge spectroscopy (XANES), J. Guzman and B.C. Gates, from The University of California, USA, *Journal of Physical Chemistry B* 2002, **106**(31), 7659-7665.

One sample initially contained gold predominantly in the form of clusters approximated as Au6 on the basis of the EXAFS data showing first- and second-shell Au-Au coordination nos. of 4.0 ± 0.4 and 1.0 ± 0.1, respectively. The other sample initially contained larger clusters, with an average diameter of about 30 .ANG. (containing about 100 atoms each, on average), as shown by the EXAFS first- and second-shell Au-Au coordination nos. of 9.4 ± 0.9 and 3.5 ± 0.4, respectively. The samples, in each of the three gases CO, O_2, and He and in the presence of CO + O_2 during CO oxidation catalysis, were investigated by EXAFS spectroscopy and XANES in a cell that was also a flow reactor. Data obtained during steady-state CO oxidation indicate the presence of gold clusters with an average diameter of about 30 .ANG., regardless of the initial size of the supported clusters. The XANES results demonstrate the simultaneous presence of both zerovalent and cationic gold in these catalysts.

2.2 Gold, Silver and Copper Catalysts Supported on TiO_2 For Pure Hydrogen Production

A catalytic study of the hydrogen production by CO water gas shift reaction (WGSR) on gold, silver and copper particles supported on TiO_2 has been carried out by F. Boccuzzi, A. Chiorino, M. Manzoli, D. Andreeva, T. Tabakova, L. Ilieva and V. Iadakiev, University of Torino, Italy, *Catalysis Today* 2002, **75**(1-4), 169-175. A deep characterisation of the catalysts by TPR and FTIR has been performed. Silver catalyst exhibits no catalytic activity, copper and gold catalysts show intermediate and very high performances, respectively. These strong differences have been interpreted on the basis of FTIR data of CO adsorption at 90 K and on the effect of coadsorbed species. Gold and copper catalysts, either oxidised or reduced, are able to adsorb CO. Reduced silver catalyst does not adsorb CO at all, while oxidised silver catalyst strongly adsorbs CO.

2.3 Bright Future for Gold Catalysts

A review by S. Carabineiro from the Leiden Institute Chemistry, Netherlands, *Chemisch2Weekblad* 2002, **98**(9), 12-13. Gold is a shiny metal that is usually regarded as being inert and consequently not suitable as a catalyst. Gold has now however acquired a reputation as a good low-temperature catalyst for a number of reactions and there is even a conference, Catalytic Gold with the theme.

2.4 Microstructural Comparison of Calcined and Uncalcined Gold/Iron-Oxide Catalysts for Low-Temperature CO Oxidation

A series of gold/iron-oxide catalysts has been prepared by an inverse co-precipitation method from a mixture of $HAuCl_4$.cntdot.$3H_2O$ and $Fe(NO_3)_3$.cntdot.$9H_2O$ by N.A. Hodge, C.J. Kiely, R. Whyman, M.R.H. Siddiqui, G.J. Hutchings, Q.A. Pankhurst, F.E. Wagner, R.R. Rajaram, S.E. Golunski from Department of Materials Science and Engineering, University of Liverpool and Johnson Matthey Research Centre, *Catalysis Today* 2002, **72**(1-2), 133-144. Samples calcined at 400°C for 3 hours exhibited poor activity towards CO oxidation whereas uncalcined materials that had only been dried at 120°C for 16 hours exhibited a far superior catalytic activity. The most active material of this latter type is shown to have 100% CO conversion at 20°C for at least 10 hours. Detailed characterisation of the dried and the calcined materials using ICP and BET analysis, XRD, HREM, STEM-EDX and Mossbauer spectroscopy has shown significant differences in their microstructure. The dried materials consist of micron scale agglomerates of 4-8 nm disordered Fe_5HO_8.cntdot.$4H_2O$ particles on which the gold is uniformly dispersed in the form of a mixture AuOOH.cntdot.xH_2O and Au_0. By comparison, the calcined materials are comprised solely of 3-5 nm cuboctahedral metallic gold particles supported on 20 nm diameter well-crystalline .alpha.-Fe_2O_3 particles. The microstructural observations and catalytic measurements are discussed in the context of the Bond-Thompson mixed Aux+/Au_0 model for the low-temp CO oxidation catalyst.

2.5 The Application of Supported Gold Catalysts to Automotive Pollution Abatement

A gold based catalyst was formulated for use as a three-way catalyst in gasoline and diesel applications by J.R. Mellor, A.N. Palazov, B.S. Grigorova, J.F. Greyling, K. Reddy, M.P. Letsoalo and J.H. Marsh, from the Anglo American Research Laboratories (Pty.) Ltd., Crown Mines, S. Africa, *Catalysis Today* 2002, **72**(1-2), 145-156. The catalyst was comprised of gold supported on cobalt oxide, which acted as promoter. The gold-cobalt oxide clusters had particle sizes of approximately 40-140 nm, and were supported on a mechanical mixture of zirconia-stabilized ceria, zirconia and titania. Under gasoline conditions at sub-stoichiometric and super-stoichiometric oxygen concentrations, fresh catalysts displayed a hydrocarbon T50 of 240°C, a CO T50 of 85°C and a NOx T50 of 310°C. After testing at temps of 500°C over periods of up to 157 h, the activity of the catalyst decreased.

3 Chemistry

3.1 Simultaneous Determination of Gold(III), Palladium(II), and Platinum(IV) with N-Phenyl-N'-(Sodium P-Aminobenzenesulfonate) Thiourea

The preparation. and characteristics of a new water-soluble reagent, N-phenyl-N'-(sodium p-aminobenzenesulfonate)-thiourea (PPT) are described, D. Ma, G. Ding and J. Wang from Henan Normal University, College of Chemistry and Environmental Science, Xinxiang, Peoples Republic of China, *Analytical and Bioanalytical Chemistry* 2002, **372**(5-6), 740-743. In the presence of cetyltrimethylammonium bromide (CTMAB) PPT reacts with Au(III), Pd(II), and Pt(IV) to form coloured complexes with absorption maxima at 317, 306.1, and 778.4 nm, respectively. Optimum conditions for colour development were studied. The reagent was used for the simultaneous detection of Au(III), Pd(II), and Pt(IV); Amberlyst A-26 macropore anion-exchange resin was used as a means of rapid seperation The method was applied to the detection of Au(III), Pd(II), and Pt(IV) in catalyst materials and anode mud with satisfactory results.

3.2 Encagement of Gold Nanoclusters in Crosslinked Resorcinarene Shells

Monolayers of resorcinarene tetraene 1 on Gold nanoclusters could be crosslinked by olefin metathesis into a nondesorptive shell. Crosslinking conditions were optimised by monitoring olefin metathesis of 1 by 1H NMR spectroscopy and obtaining empirical rate constants. S.V. Pusztay, A. Wei, K.B. Stavens and R.P. Andres from the Department of Chemistry, Purdue University, West Lafayette USA, *Supramolecular Chemistry* 2002, **14**(2-3), 291-294. Gel permeation chromatography (GPC) was found to be a useful tool for evaluating the enhanced stability of the encaged nanoparticles. Resorcinarene-encapsulated nanoparticles which were not subjected to olefin metathesis did not survive GPC analysis whereas nanoparticles in crosslinked shells were found to be stable.

4 Coatings, Films, Membranes and Wires

4.1 Femtosecond Pulsed Laser Ablation of Thin Gold Film

Laser micro machining on 1000 nm thick gold film using femtosecond (fs) laser was studied by K. Venkatakrishnan, B. Tan and B.K.A. Ngoi from the school of Mechanical and Production Engineering, Precision Engineering and Nanotechnology Centre, University of Singapore, *Optics & Laser Technology* 2002, **34**(3), 199-202. The laser pulses of 400 nm in central wavelength, 150 fs in pulse duration, and the repetition rate of 1 kHz were used for this study. Plano-concave lens with a focal length of 19 mm focused the laser beam into a spot of 3 mu.m. The sample was translated at a linear speed of 400 .mu.m/s during machining. Laser pulses of various energies were used to cut grooves on a thin gold film. The ablation depths were measured and plotted. There were two ablation regimes. In the first regime, the cutting was very shallow and the edges were free of molten material. While in the second regime, molten material appeared and the cutting edges were contaminated. Clean and precise microstructuring can be achieved with fs pulsed laser by controlling the pulse energy in the first ablation regime.

4.2 Stress-Strain Response of Free-Standing Nano-Crystalline Gold Thin-Films

Free-standing gold thin-film tension specimens of thickness in the range 500-700 nm were fabricated by e-beam deposition methods, S. Gudlavalleti, S. Kumar and L. Anand from Massachusetts Institute of Technology, *Materials Research Society Symposium Proceedings* 2002, **695** (Thin Films: Stresses and Mechanical Properties IX), 425-430. The films have grains which have thickness essentially equal to the film thickness, and an in-plane grain-size distribution which is bi-modal, with a collection of small grains with an average size of 130 nm, and another collection of larger grains with an average size of 380 nm. The films possess a strong texture with the {111} crystallographic planes aligned with the plane of the film. The thin-film specimens have been tested in simple tension using a novel-testing machine, which enables measurement of the elastic-plastic stress-strain response of the films with high resolution.

The experiments show that the gold thin-films have an initial yield strength of around 100 MPa, which is followed by rapid strain hardening to a stress level of 360 MPa at a strain of

only approximately equal to 1.2%, at which point the specimens fail abruptly. Transmission electron microscopy (TEM) investigations of the deformed films shows that the rapid strain hardening is attributable to extensive dislocation activity in the larger grains. The reason behind the low ductility in some of the gold specimens is still unclear. It may be attributable to the observed lack of dislocation activity in the smaller grains, whose boundaries then serve as easier sites for alternative inelastic mechanisms such as grain boundary sliding and de-cohesion leading to low macroscopic strains to failure.

5 Colloids and Nanotechnology

5.1 Light Interaction between Gold Nanoshells Plasmon Resonance and Planar Optical Waveguides

S. Lal, S.L. Westcott, R.N. Taylor, J B. Jackson, P. Nordlander and N.J. Halas from Rice University, Houston, USA, *Journal of Physical Chemistry B* 2002, **106**(22), 5609-5612, have studied the experimental and theoretical aspects of the interaction of gold nanoshells on a waveguiding structure. Gold nanoshells are core-shell particles consisting of a SiO_2 core surrounded by a thin gold shell. The waveguiding structure consists of a 2 .mu.m thick layer of Gold with a dielectric layer of varying thickness deposited on it.

Light scattering experiments performed on gold nanoshells randomly deposited on the dielectric layer show a change in the scattering spectrum of the nanoshells because of coupling of light with the waveguide modes. Comparison of experimental data with the oretical calculations based on the classic theory of point dipoles placed over a conducting surface, shows a significant shift in the dipole resonance position. A simple image charge calculation taking into consideration finite size effects explains the red shift observed in the experimental data for the smallest dielectric layer thickness. Observed deviations from the theoretical models are attributable to nanoshell aggregates.

5.2 Alternative Methods for the Preparation of Gold Nanoparticles Supported on TiO_2

The best current way to prepare gold/TiO_2 catalysts is the method of deposition-precipitation with NaOH (DP NaOH) developed by Haruta and co-workers. With this method it is possible to obtain small gold metal particles (2-3 nm), but the corresponding gold loading remains rather low (approximately 3 wt %). The main goal of this work, R. Zanella, S. Giorgio, C.R. Henry and C. Louis, from the Universite Pierre et Marie Curie, Paris, France, *Journal of Physical Chemistry B* 2002, **106**(31), 7634-7642, is to investigate other methods of preparation of gold/TiO_2 catalysts to obtain small gold metal particles (2-3 nm) and a higher gold loading. It is shown that anion adsorption with $AuCl_4$- (AA) does not produce gold loading higher than 1.5 wt % and the average particle size is not very small (approximately 4 nm). Cation adsorption with Au(en)23+ (CA) leads to small particles (2 nm) when the solution/support contact time is moderate (1 h), but the gold loading does not exceed 2 wt %. The most promising method of precipitation appears to be deposition-precipitation with urea (DP urea). Indeed, samples with gold particles as small as those obtained with DP NaOH (approximately 2 nm) can be prepared and all gold in solution is deposited on TiO_2 in contrast to DP NaOH. The DP urea samples reported in this paper can reach a gold loading as high as 8 wt % using a TiO_2 support with a surface area of 45 m_2 g-1. The possible mechanisms of deposition of gold on the TiO_2 support by the different methods of precipitation are discussed.

5.3 Synthesis and Properties of water-soluble Gold Colloids Covalently Derivatized with Neutral Polymer Monolayers

Citrate-capped gold nanoparticles as well as planar gold surfaces can be efficiently grafted with a covalently attached polymer monolayer a few nanometers thick, by simple contact of the metal surface with dilute aqueous solutions of hydrophilic polymers that are end-capped with disulphide moieties, These materials were characterised using: UV/Vis absorption, dynamic light scattering, and surface plasmon resonance by C. Mangeney, F. Ferrage, I. Aujard, V. Marchi-Artzner, L. Jullien, O. Ouari, E. Rekaie, A. Laschewsky, I. Vikholm and J.W. Sadowski from Ecole Normale Superieure, Paris, France, *Journal of the American Chemical Society* 2002, **124**(20), 5811-5821.

The hydrophilic polymer-coated Gold colloids can be freeze-dried and stored as powders that can be subsequently dissolved to yield stable aqueous dispersions, even at very large concentrations. They do not suffer from undesirable nonspecific adsorption of proteins while allowing the diffusion of small species within the hydrogel surface coating. In addition, specific properties of the original hydrophilic polymers are retained such as a lower critical solution temperature. The latter feature could be useful to enhance optical responses of functionalised gold surfaces toward interaction with various substrates.

5.4 Synthetic Opals Based on Silica-Coated Gold Nanoparticles

High-quality solid colloidal crystalline assemblies have been prepared by the sedimentation of monodisperse silica spheres, F. Garcia-Santamaria, V. Salgueirino-Maceira, C. Lopez and L.M. Liz-Marzan from Instituto de Ciencia de Materiales de Madrid, *Langmuir* 2002, **18**(11), 4519-4522, each containing a single gold nanoparticle in its centre. The metal centres provide a strong absorption at a well-defined wavelength that

complements the Bragg reflection arising from the periodic structure of the opal. The optical properties of these systems were characterised by transmission and specular reflectance measurements. It is clearly shown that absorption and diffraction are basically independent of each other and their relative influence can be seperated by infiltration with liquids of varying refractive index.

5.4 Oxidation of Iron in Iron/Gold Core/Shell Nanoparticles

Recently, reverse micelles were used to produce core/shell nanoparticles of iron and gold of highly uniform size distribution and reported to contain metallic iron. A composite structure of this sort is attractive in biosensor and bioactuator applications. The metallic iron core provides high magnetic sensitivity and the gold coating is easily functionalised. With iron/gold nanoparticles prepared by this method, B. Ravel, E.E. Carpenter and V.G. Harris from the Naval Research Laboratory, Washington, DC, *Journal of Applied Physics* 2002, **91**(10, Pt. 3), 8195-8197, directly measure the chemical state of the iron component using x-ray absorption spectroscopy (XAS). In earlier reports, metallicity of the iron core was inferred from magnetisation measurements rather than directly measured. In contrast, XAS directly measures the structural environment of the iron atoms. Because XAS interpretation is independent of symmetry or periodicity, it is an ideal tool for characterising nanoparticles. Using XAS, they demonstrate that the iron component of the iron/gold nanoparticles is fully oxidised. They suggest that oxidation is a persistent problem in core/shell nanoparticles of this variety and recommend that characterisation by XAS be a standard part of nanoparticle preparation.

6 Electrochemistry

6.1 An Investigation of the Electrochemical Responses of Superactivated Gold Electrodes in Alkaline Solution

It is now well established that gold, in the form of oxide-supported microparticles or even as conventional macroelectrodes, displays inexplicably high catalytic activity for some reactions. In the present work, L.D. Burke and L.M. Hurley from the Chemistry Department, University College Cork, Ireland, *Journal of Solid State Electrochemistry* 2002, **6**(2), 101-110, gold surfaces were superactivated by a combination of thermal and cathodic pretreatment. Such electrodes in base yielded up to five distinct, and quite marked, premonolayer oxidation responses within the double layer region, over the range 0.0-1.0 V (RHE). As outlined in earlier publications, such unusual behaviour is important from an electrocatalytic (and heterogeneous catalysis) viewpoint. A new mode of active site adsorption, involving highly localised electron transfer from active surface atoms to either the external circuit (in electrocatalysis) or an adsorbing reactant (in heterogeneous catalysis), is proposed. Such localised (active site) adsorption, which is based on surface quantum confinement effects, is virtually independent of (or only indirectly related to) the electronic properties of the bulk metal.

7 Electronics

7.1 Fabrication of Close-Packed TES Microcalorimeter Arrays using Superconducting Molybdenum/Gold Transition-Edge Sensors

The authors, F.M. Finkbeiner, R.P. Brekosky, J.A. Chervenak, E. Figueroa-Feliciano, M.J. Li, M.A. Lindeman, C.K. Stahle, C.M. Stahle and N. Tralshawala, from NASA/Goddard Space Flight Center, USA, *AIP Conference Proceedings* 2002, **605** (Low Temperature Detectors), 215-218, present an overview of their efforts in fabricating Transition-Edge Sensor (TES) microcalorimeter arrays for use in astronomical x-ray spectroscopy. Two distinct types of array schemes are currently pursued: 5.times.5 single pixel TES array where each pixel is a TES microcalorimeter, and Position-Sensing TES (PoST) array. In the latter, a row of 7 or 15 thermally-linked absorber pixels is read out by two TES at its ends. Both schemes employ superconducting Mo/Gold bilayers as the TES. The TES are placed on silicon nitride membranes for thermal isolation from the structural frame. The silicon nitride membranes are prepared by a Deep Reactive Ion Etch (DRIE) process into a silicon wafer. In order to achieve the concept of closely packed arrays without decreasing its structural and functional integrity, they developed the technology to fabricate arrays of cantilevered pixel-sized absorbers and slit membranes in silicon nitride films.

7.2 Spectroscopic Studies on Electrostatically Self-Assembled Gold Nanoparticulate Thin Films

Colloidal gold was prepared by citrate-induced reduction of hydrogen tetrachloroaurate. Gold nanoparticulate thin films were built up using the electrostatic self-assembly technique and characterised by different spectroscopy. (H. Yu and D. Jiang, from the Fiber Optic Sensing Technology Centre, Wuhan University of Technology, Wuhan, Peoples Republic of China *Guangpuxue Yu Guangpu Fenxi* 2002, **22**(3), 511-514) The UV-visible absorbance spectrum indicated that the gold colloid was a monodisperse suspension. The calculation using the Scherrer's equation on base of the x-ray diffraction spectrum indicated that the average size of the gold particles assembled on the substrates was approximately 21 nm. The x-ray photoelectron spectra showed that the reduction of hydrogen tetrachloroaurate was almost complete and that the gold was present in the thin films largely as gold oxide. The x-ray

photoelectron spectra also showed that the gold particles were attracted and fixed onto the PDDA-modified substrates by electrostatic forces. The UV-visible absorbance spectra and the surface enhanced Raman scattering spectra indicated that, arising from the interparticle coupling, the gold nanoparticulate thin films displayed strong collective plasma resonance absorption and surfaced enhanced Raman scattering effect.

7.3 Studies in the Electrochemical Behavior of Hydroquinone at L-Cysteine Self-Assembled Monolayers Modified Gold Electrode

L-Cysteine is combined onto gold electrode to form a self-assembled monolayers modified electrode (L-Cys/Au SAMs) by taking advantage of strong sulphur-gold interaction. ATR-FTIR, SEM, cyclic voltammetry (CV) and impedance were used by S. Wang and D. Du from the College of Chemical Material Science, Hubei University, Wuhan, Peoples Republic of China, *Sensors [online computer file]* 2002, **2**(2), 41-49, for the characterisation of the film. It shows excellent stability upon voltametric scanning and a good voltametric response towards hydroquinone with the potential ranged from 0.8 to -0.2 V (vs. SCE) in 0.5M HAc-NaAc buffer solution (pH 4.8). The oxidation potential of hydroquinone on the modified electrode shifted negative about 330 mV as compared with the bare gold electrode. The plot of catalytic current versus its concentration has a good linear relation in the range of 2.0 .times. 10-6 .approximately 2.0 .times. 10-4M with the correlation coefficient of 0.9986 and the detection limit of 4.0 .times. 10-7M by different pulse voltammetry (DPV). Mechanism for the electrocatalytical process has been studied.

8 Materials Science

8.1 Molecular Rectification: Characterization of a Dye Sandwiched Between Gold Electrodes

Langmuir-Blodgett (LB) films of the dye, 4-{2-[4-(N,N-dibutylamino)phenyl]vinyl}-N-octadecylquinolinium octadecyl sulphate, are noncentrosymetric and exhibit quadratic enhancement of the 2nd-harmonic intensity with the number of layers when corrected for absorbance, G.J. Ashwell, D.S. Gandolfo and R. Hamilton, from Cranfield University, UK, *Journal of Materials Chemistry* 2002, **12**(3), 416-420. The optimum effective susceptibility at 1.064 .mu.m, monolayer thickness and refractive indexes at the fundamental and harmonic frequencies are .chi.(2)eff = 80 pm V-1, d = 2.46 ± 0.05 nm, n.omega. = 1.51 ± 0.02 and n2.omega. = 1.65 ± 0.02 respectively. In addition, metal/(LB film)/metal devices of the dye exhibit asymetric current-voltage characteristics and, under forward bias, the current increases exponentially with the electric field. The behaviour is attributed to molecular rectification, the assignment being unambiguous for oxide-free gold electrodes.

9 Medical and Dental

9.1 Protein Adsorption and Human Osteoblast-Like Cell Attachment and Growth on Alkylthiol on Gold Self-Assembled Monolayers

Protein adsorption and growth of primary human osteoblasts on self-assembled monolayers of alkylthiols on gold (SAMs) with carboxylic acid and hydroxyl and Me termini were investigated by C.A. Scotchford, C.P. Gilmore, E. Cooper, G.J. Leggett and S. Downes, from the School of Biomedical Sciences, Queen's Medical Centre, University of Nottingham Medical School, Nottingham, UK, *Journal of Biomedical Materials Research* 2002, **59**(1), 84-99. Single-component SAMs and SAMs patterned by photolithography techniques were used. Cell growth on patterned SAMs demonstrated preferences for one pattern region in all combinations of alkylthiols, with the hierarchical preference COOH > OH > CH_3. Patterned SAMs and immunochemical were used to investigate adsorption of fibronectin and albumin with respect to different alkylthiol termini. Fibronectin adsorption from both pure solution and serum containing cell culture medium (SDMEM) followed the sequence COOH > OH > CH_3. Albumin adsorption from pure solution followed the sequence OH > COOH > CH_3; from SDMEM the sequence was CH_3 > OH > COOH. Cell attachment to SAMs with the above termini, after preadsorption with fibronectin, albumin, or mixtures of fibronectin and albumin, was measured. Attachment was maximal on COOH-terminated SAMs precoated with fibronectin. Attachment to COOH was significantly reduced only when fibronectin was omitted from the protein preadsorption solution. On OH and CH_3 SAMs increasing the proportion of albumin in the solution was sufficient to significantly reduce cell attachment. The distribution vinculin and the integrins .alpha.5.beta.1 and .alpha.v.beta.3 indicated that focal contact formation by cells varied with alkylthiol termini in the following sequence: COOH > OH > CH_3.

9.2 Gastrointestinal Persorption and Tissue Distribution of Differently sized Colloidal Gold Nanoparticles

The gastrointestinal uptake of micro- and nanoparticles has been the subject of recent efforts by J.F. Hillyer and R.M. Albrecht from the Department of Animal Health and Biomedical Sciences, School of Veterinary Medicine, University of Wisconsin-Madison, USA, *Journal of Pharmaceutical Sciences* 2001, **90**(12), 1927-1936, to develop effective carriers that enhance the oral uptake of drugs and vaccines. Here, the authors used correlative instrumental neutron activation analysis and electron microscopy to study quantitatively and qualitatively the gastrointestinal uptake and subsequent tissue/organ

distribution of 4, 10, 28, and 58 nm diameter metallic colloidal gold particles following oral administration to mice. In their quantitative studies they found that colloidal gold uptake is dependent on particle size: smaller particles cross the gastrointestinal tract more readily. Electron microscopic studies showed that particle uptake occurred in the small intestine by persorption through single, degrading enterocytes in the process of being extruded from a villus. This they claim is the first report, at the ultrastructural level, of gastrointestinal uptake of particulates by persorption through holes created by extruding enterocytes.

9.3 Gold Derivatives for the Treatment of Cancer

E.R.T. Tiekink from the Department of Chemistry, National University of Singapore, *Critical Review in Oncology/Hematology*, 2002 **42** 225-248 has investigated Gold(I) thiolates and there analogues, which have been used in the treatment of rheumatoid arthritis, against various tumours. The analogues of gold(I) thiol have been found to be more potent. In particular analogues featuring a linear P-Au-S arrangements in which the thiolate ligand is derived from a biologically active thiol display high potency. Further, targeting mitochondria with tetrahedrally coordinated gold(I) phosphine compounds with enhanced hydrophilicity is a research direction with exciting potential. Recent research has shown that gold(III) compounds featuring square planar geometries, as found in cisplatin, may target DNA and provide new anti-tumour agents.

10 Metallurgy

10.1 Gold-Base Alloys for Stomatology

The invention by E.I. Rytvin, V.V. Vasekin, S.D. Levchenko, G.S. Stepanova, D.S. Tykochinskii, I.Y. Lebedenko, I.V. Zolotnitskii and A.I. Lebedenko, Russian Patent, RU 2172159, C2, 20 August 2001, pertains to metallurgy, more particularly noble metal-base alloys, and structural material for dentures. A gold-base alloy comprises, wt %: gold, 85-86; platinum 9-10; palladium, 4-5; copper, 0.5-1 and tin, 0.5-1, total platinum to palladium ratio being 13-14 wt % and copper to tin ratio being 1:1. The alloy further comprises one or more metals from the group consisting of rhodium, ruthenium, zirconium and zinc in amt. not higher than 0.3 wt %. This provides greater hardness, improved adhesion properties and optimal k.t.p. values which makes it possible to use a wide range of both imported and domestic ceramic coatings.

11 Refining

11.1 Cyanide Control in the Metallurgical Process of Gold Extraction in Anglogold (S.A.)

AngloGold South Africa region currently consists of twelve gold plants. These plants use a combined total of $20 million of cyanide per annum. Of this, the major portion (60%) is consumed at two Ergo dump retreatment plants. Historically the primary motivation for cyanide control at Ergo has been one of leach/cost optimisation. However, more recently, with the increased public awareness of cyanide in the environment, a secondary but increasingly important motivation for control has been to ensure that only the minimum amount of cyanide is added to the process while not compromising leach performance. Following a brief overview of the Ergo process, the methodology in detecting the amount of cyanide to be added is described by B.J. Vorster and S.R. Flatman from AngloGold SA Metallurgical Technical Services, S. Afr, *Journal of the South African Institute of Mining & Metallurgy* 2001, **101**(7), 359-365.

The paper then traces the developments in cyanide control from very basic manual systems to the current automated control system. In line with the increasingly sophisticated control systems, developments also took place in regards to the method of cyanide analysis. The development of these analysers is also discussed. While cyanide is one of the major drivers, if not the major driver of gold dissolution, it cannot be viewed in isolation particularly with respect to the relationship between cyanide and oxygen as ascertained from the Elsner's well-known equation. Consequently, in order to control cyanide addition, knowledge of the relative cyanide/oxygen profiles is necessary. Various means investigated at Ergo for pulp oxygenation have therefore been included for the sake of completeness. Finally a comparison is made of the control achieved from the current system compared to the original manual system. The knowledge and experience gained at Ergo is now being used to draw up guidelines for the installation and optimisation work at the other AngloGold plants. The net effect of this will be reduced cyanide consumption for the region, which also, apart from the obvious economic benefits, translates into a reduced environmental risk.

11.2 Recovery of Gold from Polymetallic Concentrate Magnetic-Liquid and Centrifuge Separation.

The technology scheme for gold recovery from polymetallic nonferrous concentrates was developed at the Central Scientific Research Institute of tin. A.A. Shishkov, A.M. Budanov and Y.A. Orlov, *Gornyi Zhurnal* 2002, (**2**), 62-64. The sequence of the technology operations is listed as classification, gravity separation on shaking tables and centrifuge, magnetic separation and magnetic liquid separation. The overall gold recovery in optimum conditions is 98-99%.

11.3 New Method of Gold Recovery from Ore Tailing Sands by Combined Gravity Separation and Magnetic Mineral Trap Layer.

Recovery of dispersed gold from sands and ore tailings was improved by combined gravity and magnetic mineral trap layer. I. Kovlekov, *Gornyi Zhurnal* 2002, (**2**), 47-50 . On the bottom of a conventional sluice a layer magnetic and weak magnetic minerals are held by a magnetic field. The layer of magnetic minerals is acting as a trap of fine gold particles eliminating their loss in the turbulent water flow.

11.4 Bioleaching of Refractory Gold Ore(III)-Fluid Leaching Jinya Refractory Gold Concentrate by Thiobacillus Ferro-oxidans

A novel fluidised-bed reactor was designed and installed for bioleaching in a semi-continuous way, by which a process for bioleaching-cyanidation of Jinya refractory gold arsenical concentrate was studied by X. Min, L. Xiao-bo, L. Chai, W. Chen, Z. X. Yu, C. Zhang, Z. Kuang, from Department of Metallurgical Science & Engineering, Central South University, Changsha, Peoples Republic of China, *Transactions of Nonferrous Metals Society of China* 2002, **12**(2), 334-339.

The arsenic extraction rate reaches 82.5% after 4-day batch bio-oxidation of the concentrate under the optimised condition of pH 2.0, ferric ion concentration 6.5 g/L and pulp concentration 10%. The leached rate of gold in the following cyanidation is over 90%. The parameters of three series fluidised-bed reactors exhibit stability during the semi-continuous bio-leaching of the conc. Arsenic in the concentrate can be got rid of 91% after 6-day leaching. Even after 4 days, 82% of arsenic extraction rate was still obtained. The recovery rates of gold are 92% and 87.5% respectively in cyanidation from the above bio-leached residues.

11.5 The Application of Solvent Extraction to the Refining of Gold

The application of solvent extraction to the production of high-purity gold which has potential advantages over conventional refining techniques is discussed. (R.A. Grant and V.A. Drake from the Johnson Matthey Technology Centre, Reading, UK *International Solvent Extraction Conference, Cape Town, South Africa, Mar. 17-21*, 2002, 940-945 Publisher: South African Institute of Mining and Metallurgy, Marshalltown, S. Africa) A wide range of reagents have been reported in the literature for the extraction of gold, but these have limitations particularly with selectivity and ease of stripping. A simple com. alc., 2-ethylhexanol, offers significant advantages including high selectivity over other metal impurities, ability to be stripped with water at ambient temperatures, high capacity and low cost. The development of a continuous solvent extraction process is described, and initial pilot plant results are presented.